

PATENT ABSTRACTS OF JAPAN

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(54) NONAQUEOUS BATTERY

$LixAyMOz$

(57)Abstract:

PURPOSE: To improve cycle properties by using specified lithium composite oxide as a positive electrode active material.

CONSTITUTION: A specified oxide having the formular I is obtained by mixing oxides, hydroxides, carbonates, nitrates, organic acid salts, etc., of each metal of Li, A, and M and then sintering at 600-1000°C, preferably 800-960°C, in air or oxygen atmosphere. Using the resulting material as a positive electrode active material, the cycle properties are improved remarkably and excellent over charging properties are obtained. In the formular I, A stands for rubidium or cesium; M stands for metal mixture of mainly cobalt containing a few amount of nickel and/or manganese; $0.20 \leq A \leq 1.10$; $0.01 \leq M \leq 0.30$; $1.95 \leq z \leq 4$.

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CLAIMS

[Claim(s)]

[Claim 1] Li_xAyMO_z (A shows what mixed one of a rubidium and caesium, or both, and M makes cobalt or cobalt a subject, and even if there are little nickel and manganese, it expresses a little **** mixing metal for a kind.) $x -- 0.20 \leq x \leq 1.10$ and $y -- 0.01 \leq y \leq 0.30$ and $z --$ each number of $1.95 \leq z \leq 2.45 --$ it is -- the nonaqueous rechargeable battery used as positive active material.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the rechargeable battery which was excellent in especially the cycle property, and was excellent in the overcharge property about a new rechargeable battery.

[0002]

[Description of the Prior Art] From before, nonaqueous rechargeable batteries are a high voltage and a high energy consistency compared with a water-solution system rechargeable battery, and excelling in self-discharge etc. is expected very much. That is, instead of the conventional lead cell, the nickel cadmium cell, etc., the cell of the new mold using the intercalation of a stratified compound attracts attention.

[0003] For example, a cull scorch night system compound is mentioned as an example using the intercalation of a stratified compound. for example, Li_xTiS_2 and Li_xMoS_3 etc. -- although the cull scorch night system compound positive electrode had the comparatively excellent cycle nature, even when the metal lithium which has **** potential was used for a negative electrode, practical discharge voltage was before and after 2V at most, and was not necessarily satisfactory in respect of the high electromotive force which is one of the descriptions of a nonaqueous cell.

[0004] Moreover, although the positive active material using the multiple oxide containing alkali metals, such as sodium and a potassium, is reported by EP-B 1-0017400 and US-4497726 grade regardless of the lithium multiple oxide, the example using alkali metals with a still bigger ionic radius, such as a rubidium and caesium, is not known.

[0005] On the other hand, when the lithium multiple oxide which uses vanadium, manganese, cobalt, nickel, etc. as a central metal is used as positive active material, it is observed in that high electromotive force is acquired. The high electromotive force beyond 3V is acquired, and especially the nonaqueous rechargeable battery that uses as positive active material the lithium currently indicated by JP,55-136131,A, JP,62-90863,A, JP,63-121258,A, etc., and transition metals and the multiple oxide which will consist of non-transition metals etc. if it requires further has very high energy density, and is expected very much as a next-generation high performance rechargeable battery. Furthermore, even if the lithium multiple oxide itself has already contained the lithium as ion and it does not necessarily use a metal lithium as a negative-electrode active material

as a description at the time of using this multiple oxide as a positive electrode, it also has the description that a fuel cell subsystem can be formed, and it is expected as a cell excellent also in the field of safety.

[0006]

[Problem(s) to be Solved by the Invention] Thus, a lithium, transition metals, and the cell that used the multiple oxide with non-transition metals for the positive electrode when requiring further can be called rechargeable battery which may have the outstanding property. LiCoO_2 currently indicated by JP,55-136131,A It is a stratified compound and the structure which the lithium intercalated between the layers of cobalt oxide is taken. The charge reaction of the nonaqueous rechargeable battery using this advances, when the lithium ion of the multiple oxide of a positive electrode carries out a day intercalation. moves to a negative electrode, and discharges conversely, and a lithium ion carries out an intercalation from a negative-electrode active material to between the layers of positive active material. That is, by repeating the reaction which the lithium ion of the multiple oxide of a positive electrode frequents, charge and discharge are repeatable.

[0007] However, creation of the cell which used the metal lithium etc. as a multiple oxide and a negative-electrode active material as positive active material as mentioned above has the technical problem to which a lithium etc. deteriorates with advance of charge and discharge, these become powder-like, and it becomes difficult to use it over a long period of time. Then, since it has discharge potential high as positive active material by using a carbonaceous ingredient as a negative-electrode electrode material in order to solve such a technical problem, using Li_xCoO_2 ($x=0.05-1.10$) which is a compound containing a lithium is proposed. However, even if it uses such a carbonaceous ingredient for a negative electrode, when Li_xCoO_2 ($x=0.05-1.10$) is used for a positive-electrode ingredient, it is Li_xCoO_2 by the repeat of charge and discharge. A crystal structure breaks gradually, and the amount of lithiums (the amount of dopes) which can go in and out decreases to a multiple oxide reversibly, and it becomes it with the cause of cycle degradation.

[0008] On the other hand, under the electrical potential difference beyond 4V, it decomposes, and organic electrolytes, such as annular carbonate used as an electrolyte in the above-mentioned nonaqueous rechargeable battery, generate gas, raise the internal pressure of a cell, become exsorption of the electrolytic solution and the cause of breakage of a cell, and produce un-arranging practically. However, since it is the description that a nonaqueous rechargeable battery can obtain far high discharge voltage as compared with the cell which used the water solution as the electrolytic solution, the fall of practical discharge potential is not desirable.

[0009] It is safe and this invention is proposed for the purpose of the thing which can prevent degradation of the positive active material by the repeat of the charge and discharge of the above nonaqueous rechargeable batteries, and can repeat charge and discharge for a long period of time, and can control the generation of gas at the time of overcharge and for which a reliable nonaqueous rechargeable battery is offered.

[0010]

[Means for Solving the Problem] It finds out this invention person having few structural changes, even if the multiple oxide which permuted some lithiums of lithium cobalt oxide in one of a rubidium and caesium or both repeats charge and discharge, as a result of inquiring wholeheartedly, and being excellent in cycle nature, in order to solve the above-

mentioned trouble, and excelling in a overcharge property, and came to complete this invention. That is, this invention is $\text{Li}_x\text{A}_y\text{MO}_z$ (A shows one of a rubidium and caesium, or both mixed metal, and M makes cobalt or cobalt a subject, and even if there are little nickel and manganese, it expresses a little **** mixing metal for a kind.). $x \rightarrow 0.20 \leq x \leq 1.10$ and $y \rightarrow 0.01 \leq y \leq 0.30$ and $z \rightarrow$ each number of $1.95 \leq z \leq 2.45$ -- it is -- the nonaqueous rechargeable battery used as positive active material -- it is going to provide -- it is a thing.

[0011] Hereafter, this invention is explained to a detail. Above $\text{Li}_x\text{A}_y\text{MO}_z$ is obtained by calcinating 600-1000 degrees C preferably in air and under an oxygen ambient atmosphere in a 800-960-degree C temperature requirement, after making the oxide of the metals of Li, A, and M, a hydroxide, a carbonate, a nitrate, an organic-acid salt, etc. mix. Although especially the permutation ratio of a rubidium or caesium is not restricted here, if discharge capacity and the rate of self-discharge are taken into consideration, it is desirable that they are 1% or more and 30% or less to cobalt. They are 2% or more and 20% or less more preferably.

[0012] Although it is not yet clear about the effectiveness of the permutation of alkali metal, it is possible by permuting by the rubidium with a bigger ionic radius than a lithium, and caesium that distortion, the intercalation of a lithium, and a day intercalation become [a crystal structure] easy moderately. Consequently, at a moderate permutation rate, cell capacity increases greatly. Furthermore, a rubidium and caesium work effectively to maintenance of the crystal structure at the time of a lithium carrying out a day intercalation, prevent degradation of positive active material, the cycle nature of a rechargeable battery is raised remarkably, and control the rapid power surge at the time of overcharge, prevent too much generation of gas, and raise a overcharge property.

[0013] In the lithium multiple oxide shown by the general formula $\text{Li}_x\text{A}_y\text{CoO}_z$ used as positive active material by this invention, A shows the metal which mixed one of a rubidium and caesium, or both at a rate of arbitration. M makes cobalt or cobalt a subject, and even if there are little nickel and manganese, it expresses a little **** mixing metal for a kind. Small quantity means extent 30% or less to cobalt here.

[0014] Moreover, the value of x is changed according to a presentation, a charge condition, and a discharge condition, and the range is $0.20 \leq x \leq 1.10$. Although the day intercalation of a lithium ion happens by charge and the value of x becomes small, it becomes impossible to hold the crystal structure and stops namely, showing the engine performance as positive active material or less by 0.20. Moreover, the value of y is $0.01 \leq y \leq 0.30$, and is not fundamentally changed by charge and discharge. When the value of y exceeds less than 0.01 and 0.30, the fall of discharge capacity and cycle nature, the increment in the rate of self-discharge, and the generation of gas at the time of overcharge increase, phenomena, like a overcharge property worsens occur, and it is not desirable.

[0015] Moreover, the range of the value of z is $1.95 \leq z \leq 2.45$, and it is changed by the ambient atmosphere at the time of baking, and the presentation ratio of alkali metal. The amount of dopes as used in the field of [again] this invention means the amount of lithiums which moves reversibly at the time of charge and discharge, and the amount of dopes used in an example means reversibly [the lithium in a multiple oxide] what% it moves on the basis of cobalt.

[0016] When creating a positive electrode using the multiple oxide of this invention, an

organic polymer can also be used as a binder. In that case, the approach using the thing which made the binder solution made to dissolve this organic polymer in a solvent distribute an electrode active material as coating liquid and the approach using the thing which made the water emulsification dispersion liquid of this organic polymer distribute an electrode active material as coating liquid, the approach of applying the solution and/or dispersion liquid of this organic polymer to the electrode active material by which preforming was carried out beforehand, etc. are mentioned as an example. although especially the amount of binders to be used is not what is limited -- usually -- the electrode active material 100 weight section -- receiving -- 0.1 - 20 weight section -- it is the range of 0.5 - 10 weight section preferably.

[0017] Although especially the organic polymer used here is not limited, when specific inductive capacity [in / in this organic polymer / 25 degrees C and the frequency of 1kHz] has 4.5 or more values, especially, a desirable result is brought about and it has the property excellent in fields, such as cycle nature and an overvoltage, especially as cell engine performance. If an example of the organic polymer which fulfills these conditions is shown, polymers, such as acrylonitrile, meta-chestnut nitril, and vinyl fluoride, vinylidene fluoride, a chloroprene, and a vinylidene chloride, or a copolymer, a nitrocellulose, cyanoethyl cellulose, polysulfide rubber, etc. will be mentioned.

[0018] It faces manufacturing an electrode by this approach, and is fabricated by carrying out spreading desiccation of said coating liquid on a base material. If it requires at this time, you may fabricate with a charge collector ingredient, and charge collectors, such as aluminum foil, a nickel foil, a titanium foil, copper foil, an SUS foil, and a molybdenum foil, can also be used as a base material as an exception method. Although said binder, an electric conduction adjuvant, other additives, for example, a thickener, a dispersant, an extending agent, an adhesion adjuvant, etc. may be added by the cell electrode manufactured using the active material of this invention, that in which the active material of this invention is contained 25% of the weight or more at least is said. As an electric conduction adjuvant, a metal powder, electric conduction metallic-oxide powder, carbon, etc. are mentioned. Especially addition of this electric conduction adjuvant can find out remarkable effectiveness, when using the active material of this invention. Especially carbon gives a desirable result, the fall effectiveness of a remarkable overvoltage is usually discovered to the active material 100 weight section with addition of 1 - 30 weight section, and the outstanding cycle nature is demonstrated.

[0019] Although carbon here does not mean the carbon which the property that negative-electrode carbonaceous ingredients differ is required, and was not necessarily specified, graphite, carbon black, etc. are mentioned as an example. When carbon of 0.1-10 microns of mean diameters and carbon of 0.01-0.08 microns of mean diameters are especially mixed and used as desirable combination, the especially excellent effectiveness is given.

[0020] although especially the negative-electrode active material used by this invention is not what is limited -- a metal lithium, a lithium alloy, $\text{Li}_x\text{Fe}_2\text{O}_3$, and Li_xWO_2 etc. -- carbonaceous system ingredients, such as conductive polymer negative electrodes, such as a metallic-oxide negative electrode, polyacethylene, and Polly p-phenylene, pitch system carbon, and a vapor growth carbon fiber, etc. are mentioned. The outstanding effectiveness is demonstrated when the matter which can intercalate lithium ions, such as a carbonaceous ingredient, especially is used for a negative electrode.

[0021] The electrode using the active material of said this invention as a basic component

in the case of assembling the nonaqueous rechargeable battery of this invention and also a separator, and nonaqueous electrolyte are mentioned. Although are not limited especially as a separator, and textile fabrics, a nonwoven fabric, a glass cloth, the synthetic-resin fine porosity film, etc. are mentioned, when using a thin film and a large area electrode, the synthetic-resin fine porosity film indicated by JP,58-59072,A, especially the polyolefine system fine porosity film are desirable in respect of thickness, reinforcement, and membrane resistance.

[0022] although not limited especially as an electrolyte of nonaqueous electrolyte, if an example is shown -- LiClO_4 , LiBF_4 , LiAsF_6 , $\text{CF}_3\text{SO}_3\text{Li}$, LiPF_6 , LiI , LiAlCl_4 , NaClO_4 , NaBF_4 , NaI , $4(\text{n-Bu})\text{N}^+\text{ClO}_4$, $4(\text{n-Bu})\text{N}^+\text{BF}_4$, and KPF_6 etc. -- it is mentioned. Moreover, as an organic solvent of the electrolytic solution used, although ether, ketones, lactone, nitril, amines, amides, a sulfur compound, chlorinated hydrocarbons, ester, carbonate, a nitro compound, a phosphoric ester system compound, a sulfolane system compound, etc. can be used, for example, ether, ketones, lactone, nitril, ester, chlorinated hydrocarbons, carbonate, and a sulfolane system compound are desirable also among these. Furthermore, it is the mixture of annular lactone, or an annular lactone and annular carbonate preferably.

[0023] As these examples of representation, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1,4-dioxane, an anisole, mono-glyme, an acetonitrile, Propionitrile, 4-MECHIRU 2-pentanone, butyronitrile, Valeronitrile, a benzonitrile, 1,2-dichloroethane, gamma-butyrolactone, Dimethoxyethane, a methyl FORU mate, propylene carbonate, Although ethylene carbonate, vinylene carbonate, dimethylformamide, dimethyl sulfoxide, a dimethyl thio formamide, a sulfolane, 3-MECHIRU sulfolane, trimethyl phosphate, phosphoric-acid triethyl, these mixed solvents, etc. can be mentioned It is not necessarily limited to these.

[0024] Furthermore, if it requires, a cell is constituted using components, such as a charge collector, a terminal, and an electric insulating plate. Moreover, it is [0025] to which the gestalt of a positive electrode, a negative electrode, the paper mold cell that used the separator as the monolayer or the double layer when requiring further, a laminating mold cell or a positive electrode, a negative electrode, the cylindrical cell around which the separator was wound in the shape of a roll when requiring further is mentioned as an example especially as structure of a cell although not limited.

[Example] Hereafter, although an example and the example of a comparison explain this invention in more detail, it is not limited to these examples.

[0026]

[Example 1] After mixing a lithium carbonate, a carbonic acid rubidium or cesium carbonate, and cobalt oxide by the predetermined mole ratio, the multiple oxide $\text{Li}_x\text{AyCoO}_z$ was obtained by calcinating at 930 degrees C in air for 3 hours. This multiple oxide is rinsed after grinding with a ball mill, and it dries, and is $\text{Li}_{0.9}\text{Cs}_{0.1}\text{CoO}_2$ with a mean particle diameter of 15 microns or less. It considers as positive active material. Make graphite and acetylene graphite into an electric conduction agent, and a fluororubber is used as a binder. respectively -- $\text{Li}_{0.9}\text{Cs}_{0.1}\text{CoO}_2$: graphite: -- acetylene black: -- what was mixed by the weight ratio of fluororubber = 100:7.5:2.5:2 It mixed in the dimethylformamide solution of a polyacrylonitrile and the sheet which carried out spreading desiccation was used as the positive electrode as the shape of a paste at aluminum foil. Moreover, what was mixed by the weight ratio of needle

coke:fluororubber =95:5 was mixed in the dimethylformamide solution of a polyacrylonitrile, as the shape of a paste, the sheet which carried out spreading desiccation was used as the negative electrode at nickel foil, Li metal was made [needle coke powder was used as the negative-electrode active material, the fluororubber was used as the binder,] into the reference pole, and the cell shown in drawing 1 was manufactured. In addition, the polypropylene nonwoven fabric was used as a separator 7, and the liquid which adjusted hoe lithium fluoride to the concentration of 1.0M was used for the mixed solvent (volume ratio = 1:1) of propylene carbonate and gamma-butyrolactone as the electrolytic solution.

[0027] 1.0 mA/cm² after charging this cell by constant-voltage 4.2V for 7 hours It discharged on termination electrical-potential-difference 2.7V conditions by constant current. Change of the discharge capacity at the time of repeating this charge-and-discharge cycle is shown in drawing 2 . Moreover, the discharge capacity (weight criteria) of 1 cycle eye, the amount of dopes of cobalt criteria, and the discharge capacity rate (%) to 1 cycle eye of a 100 cycle eye are combined as cycle nature, and are shown in Table 1.

[0028] Moreover, it is this cell 5.0 mA/cm² The electrical-potential-difference change when charging by constant current is shown in drawing 3 .

[0029]

[The example 1 of a comparison] LiCoO₂ positive active material -- carrying out -- graphite and acetylene black -- an electric conduction agent -- carrying out -- a fluororubber -- a binder -- carrying out -- each LiCoO₂ : graphite: -- acetylene black: -- mixed what was mixed by the weight ratio of fluororubber =100:7.5:2.5:2 in the dimethylformamide solution of a polyacrylonitrile, considered as the shape of a paste, and the sheet which carried out spreading desiccation was used as the positive electrode at aluminum foil, and also the same cell as an example 1 was manufactured, and same evaluation was performed. The electrical-potential-difference change when carrying out constant-current charge of the change of the discharge capacity accompanying a cycle to drawing 4 is shown in drawing 3 .

[0030] it illustrated for the example 1 of a comparison -- as -- LiCoO₂ **** -- Li_{0.9} Cs_{0.1} CoO₂ illustrated in the example 1 to discharge capacity falling even to 53.7% in 100 cycles 87.4% and good cycle nature were shown in the case. Moreover, it follows on cycle nature and is LiCoO₂. It is Li_{0.9} Cs_{0.1} CoO₂ to an overvoltage being remarkable then (it being 0.4V in 100 cycle), and increasing. It had stopped about 0.05V and at a slight increment at the case.

[0031] Moreover, it compares, although the power surge beyond 5V is loose when behavior differs clearly and it contains caesium by the existence of caesium, and the electrical-potential-difference change at the time of constant-current charge is LiCoO₂. A power surge then rapid from the 5V neighborhood happens, and a lot of gas occurs in connection with it.

[0032]

[Examples 2-4] It completely carried out similarly except having changed as Cs content of the positive active material of an example 1 was shown in Table 1 in the example 1. A result is shown in Table 1.

[0033]

[Examples 5-7] It completely carried out similarly except having permuted Rb instead of

Cs of positive active material in examples 1-4. A result is shown in Table 2.

[0034]

[Example 8] It sets in the example 1 and is $\text{Li}_{0.9}\text{Cs}_{0.1}\text{CoO}_2$. It is $\text{LiCs}_{0.1}\text{CoNi}_{0.1}\text{O}_2$ to instead of. It completely carried out similarly except having used. A result is shown in Table 3.

[0035]

[Example 9] It sets in the example 1 and is $\text{Li}_{0.9}\text{Cs}_{0.1}\text{CoO}_2$. It is $\text{LiCs}_{0.1}\text{CoMn}_{0.1}\text{O}_2$ to instead of. It completely carried out similarly except having used. A result is shown in Table 3.

[0036]

[Example 10] The polyacetylene negative electrode was used as a negative electrode, and also it carried out completely like the example 1. A result is shown in Table 4. The method of preparation of a polyacetylene negative electrode is as follows. N_2 Toluene 50ml was taken to the glassware of 800ml of content volume under the ambient atmosphere, tetrabutoxytitanium 6ml and triethylaluminum 10ml were added, and the catalyst was prepared. The inside of a system after cooling a container at -78°C was exhausted, catalyst liquid was applied to the container wall surface, and acetylene gas was introduced. Film-like polyacetylene generated on the wall surface immediately, and the inside of an after [15 minute neglect] system was exhausted. After after [washing] 0.5N-HCl-MeOH washed 5 times with toluene, it dried and took out.

[0037] It used, after heat-treating this film-like polyacetylene for 5 seconds at 250°C .

[0038]

[The example 2 of a comparison] The polyacetylene negative electrode was used as a negative electrode, and also it carried out completely like the example 1 of a comparison. A result is shown in Table 4.

[0039]

[Table 1]

	組 成	放 電 容 量 AH/Kg	ドープ量 %	サイクル性 %
実施例1	$\text{Li}_{0.9}\text{Cs}_{0.1}\text{CoO}_2$	140.3	57.8	87.4
比較例1	LiCoO_2	142.8	52.2	53.7
実施例2	$\text{Li}_{0.98}\text{Cs}_{0.02}\text{CoO}_2$	141.9	53.2	82.6
実施例3	$\text{Li}_{0.95}\text{Cs}_{0.05}\text{CoO}_2$	140.4	54.6	86.8
実施例4	$\text{Li}_{0.8}\text{Cs}_{0.2}\text{CoO}_2$	112.6	51.7	79.1

[0040]
[Table 2]

	組 成	放 電 容 量 AH/Kg	ドープ量 %	サイクル性 %
実施例5	$\text{Li}_{0.98}\text{Rb}_{0.02}\text{CoO}_2$	139.4	51.7	79.6
実施例6	$\text{Li}_{0.95}\text{Rb}_{0.05}\text{CoO}_2$	136.7	51.9	81.3
実施例7	$\text{Li}_{0.9}\text{Rb}_{0.1}\text{CoO}_2$	129.8	47.5	81.7

[0041]
[Table 3]

	組 成	放 電 容 量 AH/Kg	サイクル性 %
実施例 8	$\text{LiCs}_{0.1}\text{CoNi}_{0.1}\text{O}_2$	139.1	84.6
実施例 9	$\text{LiCs}_{0.1}\text{CoMn}_{0.1}\text{O}_2$	137.9	82.1

[0042]

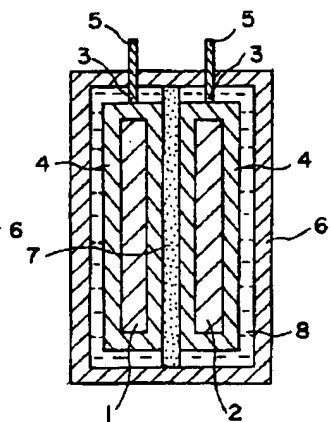
[Table 4]

	放 電 容 量 AH/Kg	ドープ量 %	サイクル性 %
実施例 10	139.9	51.1	86.8
比較例 2	142.7	58.8	54.9

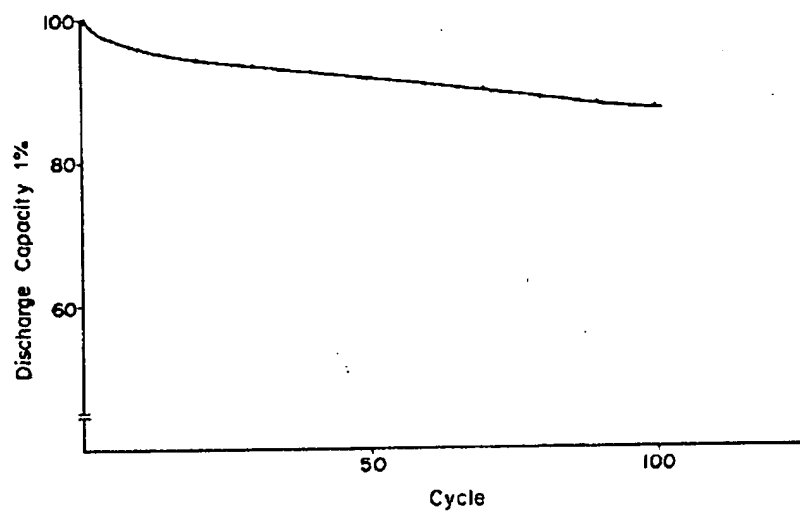
[0043]

[Effect of the Invention] The cycle property which was the fault of the conventional nonaqueous rechargeable battery is improved by leaps and bounds, and is excellent also in a overcharge property, and the cell of this invention has it. [widely / as noncommercial uses, such as an object for small cell devices, and an object for electric vehicles and an industrial power source / useful]

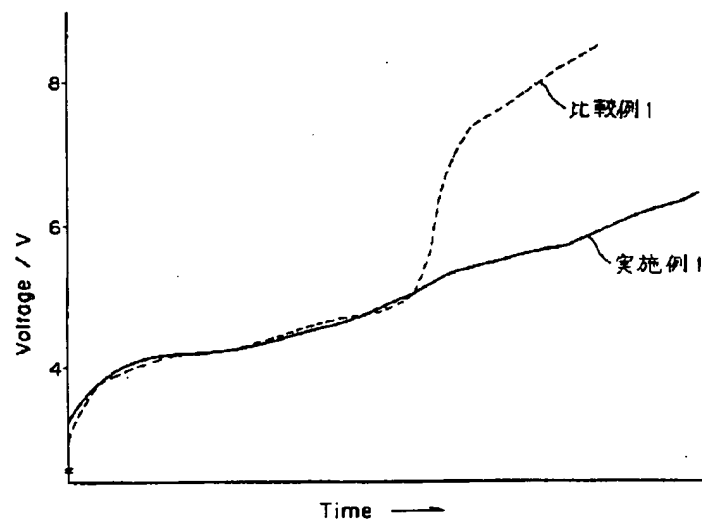
Drawing 1



Drawing 2



Drawing 3



Drawing 4

